CEMENT AND LIME MANUFACTURE

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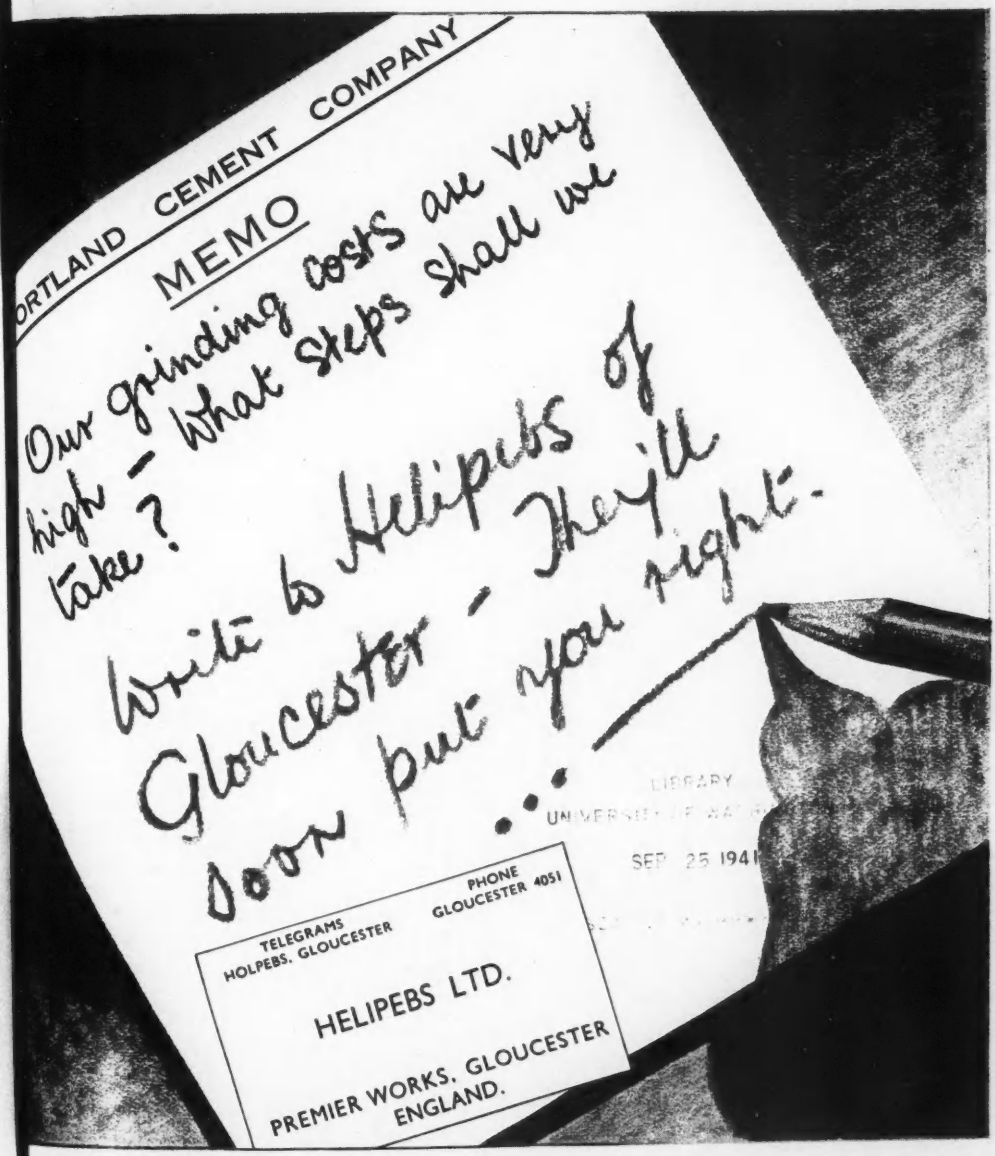
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VOLUME XIV. NUMBER 8 AUGUST 1941

Particle Size Determination by Sedimentation.

AN interesting discussion on the determination of particle sizes and on a new apparatus for the measurement of particles was given by Mr. Karl Kammermeyer (Drexel Institute of Technology, Philadelphia) and Mr. J. L. Binder (the Pure Oil Company, Chicago) recently before the American Chemical Society. The following is an abstract of the paper.

Several different experimental methods of measuring particle size by sedimentation have been used but probably the simplest is that used by Kelly and others ([2,5]), which consists essentially of measuring the change in pressure exerted by the suspension as the suspended material separates out. Generally, in order to measure small pressure changes, an inclined manometer attached to the settling tube is used.

The relationship between the pressure changes and the weight of material separated out may lead to serious errors in the determination if the physical dimensions of the apparatus are not considered. When the pressures are indicated by the positions of the meniscus in the inclined arm of the manometer, which is filled with the suspending medium, the relationship as given by Kraemer and Stamm ([4]) is

$$W_P = \frac{ds\,(S + A \sin b)}{s - d}\,(l_0 - l_t) = k_1\,\Delta l \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where W_P = weight of material that has settled out at time t, d = density of suspending medium, s = density of suspended solid, S = cross-sectional area of bore of inclined arm of manometer, A = cross-sectional area of settling tube, l_0 = meniscus reading at $t = O$, and l_t = meniscus reading at time t.

When S is so small compared with A that it can be neglected, equation (1) reduces to that given by Kelly ([2]), except that Kelly's equation gives the amount in suspension at any time.

$$W_1 = \frac{dVs \sin b}{h\,(s-d)}(l_0 - l_t) = W_0 - W_P = k_2 \Delta l \quad .. \quad .. \quad .. \quad (2)$$

where W_1 = weight of material in suspension at time t, V = volume of suspension above side tube, h = height of suspension above side tube, and W_0 = total weight of solid initially in suspension of volume V. Physically, this omission of S means that the amount of liquid entering the settling tube from the inclined arm is neglected.

If it is desired to evaluate the sedimentation data by means of equation (2), the dimensions of the apparatus have to be adjusted accordingly. This can be done by making area A very large compared with area S. But for ordinary values of S (diameter 1 to 5 mm.) this means that the apparatus will be unduly large. On the other hand, if S is made small compared with a convenient value for A, difficulties and erroneous results may be encountered because the suspending medium will move too slowly in the inclined arm owing to capillary attraction. Therefore the safest procedure is to use equation (1) in evaluating the data. Values of k_1 and k_2, obtained with an inclined manometer type of apparatus at the Drexel Institute of Technology, were 0·531 and 0·417 respectively when operating with aqueous suspensions of calcium carbonate, and with such a difference it is imperative to use equation (1).

Another relation for the weight of material separated out and the pressure changes is that given by Duncombe and Withrow [1]:

$$\% W_P = \frac{l_0 - l_t}{l_0 - l_f} \times 100 \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3)$$

where l_f = final meniscus reading. Despite its simplicity, the difficulties involved in the determination of l_f limit the general usefulness of this relationship.

Operating Variables.

An examination of equation (1) shows that the factors which are constant for any one experiment and apparatus are the densities of liquid and solid and the areas, while l_0 and l_t are the only variables that have to be measured. The various W_P's are calculated from the l readings and the sum of these values for the total settling time should equal the weight of solid initially in the suspension.

The determination of l_0 may offer some difficulties. In the determination of the total meniscus change the relationship between the initial level of the suspension and the level of the meniscus exerts considerable influence at the start of the experiment. Although the relative position of these two levels is usually approximated prior to a settling experiment, it is almost impossible to have them in their exact positions in the actual determination. Therefore the meniscus level is either somewhat above the actual level corresponding to the level of the suspension in the settling tube, or it is somewhat below the actual level. In the first case the meniscus level will drop at a rate faster than that corresponding to the settling out of particles, and in the second case it will drop

at a rate lower than the actual rate. In extreme instances of the second case the meniscus may actually be observed to stand still or even move upward for a short time. It is, therefore, necessary that the actual meniscus level be determined graphically by plotting meniscus readings against time and extrapolating to zero time. Generally, it will be found that meniscus readings below one minute are not reliable, and it may, therefore, be of advantage to take meniscus readings at intervals of 30 seconds or less in the period of about one to five minutes. This procedure should give sufficient points of the time-meniscus reading curve to permit accurate extrapolation to zero time.

The initial meniscus position can also be found from equation (1) when W_P and k_1 can be determined accurately because $\Delta l = l_0 - l_t = \frac{W_P}{k_1}$. In this case it is best to measure Δl for complete settling because then W_P is the total weight of solid in suspension.

In using equation (1) it is desirable to know W_0 in order to check the accuracy of the summation of the individual weights corresponding to the l readings. When equation (2) is used it is necessary to know W_0 accurately. If the suspension is uniform and the total volume of the settling tube and the volume of the tube above the side arm (all to the same height) are known, W_0 may be found from the weight of material put into the settling tube. In some cases, k_1 and Δl for complete settling may be found accurately enough to permit determining W_0 from equation (1). Of course, an aliquot of the suspension could be analysed, but again it would be necessary to assume a uniform suspension.

Viscosity of Suspending Medium.

The viscosity of the suspending medium is primarily determined by the largest particle size to be measured. If the viscosity of the medium is too low, particles above a certain size will settle so rapidly that differentiation will not be possible and if it is necessary to obtain closer differentiation a medium of higher viscosity must be used. The viscosity required can be approximated from Stokes's law if an estimate of the largest particle size is available. According to Knapp [3], the minimum allowable viscosity is given by

$$\mu_{\text{min.}} = \sqrt{0{\cdot}37\, r^3_{\text{max.}}\, g d\, (s - d)} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (4)$$

where $r_{\text{max.}}$ is the maximum particle radius, g is the gravitational constant, and the other terms are as previously defined.

Occasionally it was observed that the curve of weight settled against time showed a curvature which was slightly concave upward in the early part of the settling period. An analysis of a number of such curves indicated that the occurrence of this inverted section of the curves was found with solids of a wide particle size range which contained a considerable percentage of large particles. The slope of this part of a curve, of course, indicated that the reverse of sedimentation was taking place. Close observation of the settling process revealed that during the period of rapid settling—that is, in the part represented

by the steep portion of the settling curve—the liquid which returned from the semicapillary tube entered the settling tube with sufficient velocity to set up an upward current. As a consequence some particles which had settled past the level of the side arm were lifted above this level and immediately exerted an increased pressure which resulted in a slowing up of the rate of meniscus fall. Translated into the weight-time curve this means a decrease in the slope dW/dt and when normal settling is resumed a discontinuity is introduced in the settling process. The remedy for such a condition is the use of a suspending medium of higher viscosity which will retard the rate of fall of the meniscus to a point where the liquid draining from the semicapillary tube will not set up eddy currents.

Smallest and Largest Particle Sizes.

When, in a particular experiment, a suspending medium is used which has a viscosity high enough to permit accurate measurement of the fall of the majority of the particles, it will usually be found that for this medium the smallest particles settle too slowly and the largest too quickly. The size of the smallest particles can generally be found accurately enough by extrapolating the accumulation curve of weight settled out against time to complete settling and using this value of the time in the Stokes's equation. This curve becomes asymptotic to a line parallel to the time axis, but the error introduced by extrapolating to 100 per cent. settled out is small since the radii of the particles are small.

It is more difficult to arrive at the size of the largest particles. In the usual case they will generally settle so rapidly that accurate measurements cannot be made at less than one minute. As an approximation it is possible to extrapolate the curve to the origin with a straight line and in some cases this is accurate enough. A screen analysis will also indicate the upper limit of particle size. The other, more accurate, procedure is to use a medium of higher viscosity for these particles, so that the time of fall is increased sufficiently to permit accurate measurement.

New Apparatus.

The discussion of these factors shows that methods based on a moving meniscus level involve experimental difficulties which may result in appreciable inaccuracies. Furthermore, with large particle sizes these methods are of little use because suspending media of high viscosity must be used to permit accurate measurement of the time of fall of the particles. On account of the high viscosity, the liquid moves so slowly in the capillary side arm that the measurements are practically worthless.

The apparatus shown in Fig. 1 was developed in the laboratories of the Pure Oil Company. It permits the use of a suspending medium of high viscosity and with it particle sizes corresponding to 32-mesh (about 500 microns in diameter) have been measured employing an S. A. E. 40 oil as suspending medium. The settling tube is large enough to permit the introduction of a motor-driven stirrer arranged to give an upward motion to the suspension. The spoon gauge, made by elongating a thin-walled bulb and then flattening

on one side, is thin enough so that a pressure difference of a few millimetres of mercury will impart a noticeable displacement to the pointer. The optical arrangement amplifies the pointer movement. In use, the whole apparatus is filled with the suspending medium to a fixed point on the settling tube. After closing the stop-cock, a weighed amount of the material is stirred in until the suspension is uniform. Upon cessation of stirring the stopcock is opened and readings of the pointer position are taken at various times. The apparatus must be protected from thermal and mechanical changes.

The deflections of the pointer are converted to pressure changes by calibrating the gauge. This can be done, as described by Knapp [3], by immersing cylinders of known volumes in the suspending liquid in the settling tube. The

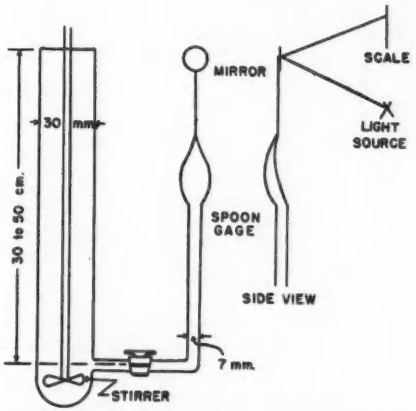

Fig. 1.—Apparatus for Determining Size of Particles.

increases in height of the liquid are converted to pressure increases and these are plotted against the corresponding pointer displacements. The resulting curve is a calibration curve of the gauge.

From the pressure changes the weight of material separated out is found by

$$\Delta P = \frac{W_P}{A}\left(1 - \frac{d}{s}\right) \quad .. \quad .. \quad .. \quad .. \quad .. \quad (5)$$

in which the symbols have the same meaning as before. Obviously the percentages settled out can be obtained also by means of equation (3). After constructing the accumulation curve, the particle size distribution curve is obtained in the usual manner.

There are many advantages of this apparatus in actual use. Since a given height h of the liquid always corresponds to a definite position l of the pointer it is apparent that, knowing the bulk density of the material (determined with the liquid which is used as the suspending medium), the final position of the pointer lf can be calculated. This corresponds to complete settling. Since there is no flow of liquid from the side arm, disturbances which can be caused in this

way in the manometer type of apparatus are eliminated. Because of the amplification of the pointer displacement, closer differentiation of particle sizes is possible. Experience has shown that this apparatus is more convenient in use than the usual type, and particle sizes of materials can be measured with it that are impossible to measure with the manometer type.

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Rate of Calcination of Limestone.

IN this journal for February, 1937, Dr. N. V. S. Knibbs discussed the rate of calcination of various sizes of limestone. His conclusions are commented on by Mr. V. J. Azbe in the May, 1941, number of *Rock Products*, from which journal we take the following abstract:

Several investigations have been conducted on the calcination rate of limestone, such as those of Haslam and Smith, Gurnas, and Block, but probably the most reliable is that of Dr. N. V. S. Knibbs. The dimension of stone having the most bearing on the calcination rate is the minimum dimension, which is different from screen size. If a 6 in. lump has only a 4 in. thickness, then for the purposes of calcination it becomes a 4 in. stone. The conclusion seems to be that a 4 in. thick slab and a 4 in. ball have the same calcination time. The curves by Dr. Knibbs (*Fig.* 1) are the most conservative; those of Haslam and of Furnas both give a much shorter calcination time. All call for a free access of heat to the limestone so that the temperature called for prevails in a form of convecting gas around the stone, which is not always the case in a lime kiln. For example, if two slabs each 3 in. thick have their faces in direct contact, with no chance for gas penetrating between, the calcination time will not be 2·6 hours at 2,200 deg. F., as shown by the chart, but rather that of a 6 in. piece, or 8 hours.

If the kiln charge were made up of uniform-sized balls, non-spalling, non-sanding, and not subject to crushing, then the passages would remain free, an ideal state would prevail, and the rate of calcination would correspond to those given by the chart and kiln capacity would be at the maximum. However, the conditions within any lime kiln are far from ideal due either to crushing of lime under load or its natural sanding or spalling. Then a packed condition occurs, when relatively small pieces of calcining lime, of normally high calcining rate, become enveloped in disintegrated matter through which heat-carrying gases cannot readily penetrate. The calcining time becomes longer and small stone may require, on the average, a longer time than large stone.

Study of the chart shows that stone of half size requires only one-third the time for calcination, and so we may hastily assume that potential capacity under

ideal conditions would be trebled. But that would be a false assumption. It is not the surface of the lime in the kiln that counts but rather the calcination surface—the surface along the boundary between calcium carbonate and the calcium oxide ; this line in an active kiln progresses continually, and as it does the surface diminishes to disappear when the centre is reached.

In any normally functioning kiln the measure of activity would be the amount of calcining surface in the hot zone at any given moment ; this is the surface within the lump at the boundary of the two phases, and not the outer surface of

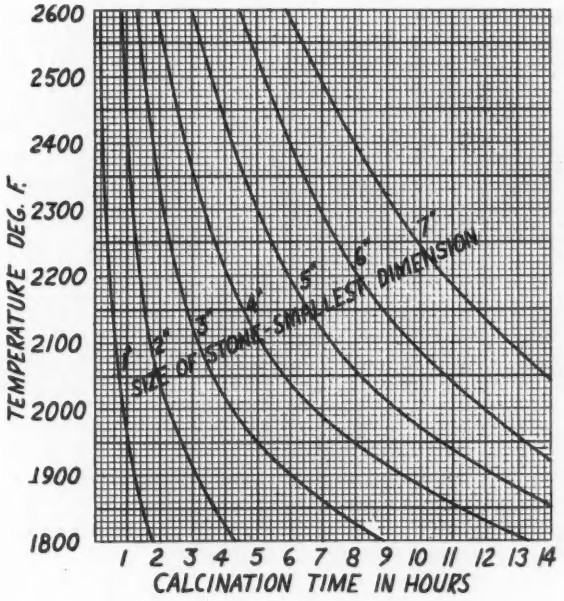

Fig. 1.—Rate of Calcination of Limestone.

the lump. The capacity of any kiln section at a particular temperature will be proportional to the amount of this calcination surface. Before a 6 in. lump of limestone is calcined it is reduced to 3 in., and as a 3 in. lump the calcining surface is only 25 per cent. ; therefore if we had started with half-size stone the calcining surface in any kiln section would be four times as great. But as a 3 in. piece is only 12·5 per cent. of a 6 in. piece in weight, the amount of calcining matter, for example, in the finishing zone of a kiln is only one-eighth when stone of 6 in. compared with 3 in. is used. The balance of the space at this point would be occupied by the lime. This means a waste of kiln space which is, in a measure, distinct from the rate of calcination. Lumps of 3 in. will burn in one-third the time of 6 in. lumps, but, when they are present as core, the finishing zone will

contain only one-eighth the weight of the unacted-upon limestone, and the rest would be better on its way out if that were possible.

Furnas claims that the penetration rate of the calcination zone is constant for any given temperature. This would mean that, in a period of four hours, during the first hour 59·6 per cent. would be calcined; in the second hour, 29·6 per cent.; in the third hour 9·1 per cent.; and in the last hour only 1·1 per cent. If the penetration zone of calcination were actually constant, then Dr. Knibbs's curves would be straight lines, which they are not. Contrary to Furnas's claims that 3 in. core requires the same calcining period as a 3 in. piece of stone, it actually requires considerably more. The lime-kiln hot zone space where the 3 in. core is burnt-out is even worse; not only because its volume contains one-eighth limestone, but this limestone is insulated and heat has difficulty of access.

Prevailing high temperatures are helpful, but temperatures are high because heat generation is faster than heat absorption. There is too little stone and heat has too great a difficulty of access, but combustion with preheated air coming up in the cooler is going on, and so there is little wonder if damage to walls may occur and lime surfaces become overburned.

From a capacity standpoint everything is in favour of smaller stone; certainly 3 in. in preference to 6 in. But small stone in a kiln with any given draught will not give as high a capacity as large stone, in spite of its calcining rapidity. For straight spall burning certain modifications are necessary, and these depend not only on the initial size of stone but also on how the lime will retain its original size as it passes through the kiln. For any given kiln height the draught for an equal flow of gas will be four times as great when stone size is reduced to half. It may even be more if the lime breaks up, because it is easier to close the voids among 3 in. lumps than among 6 in. lumps. If the height of the charge is reduced by half, the draught is necessarily halved, but it is still twice as much as with 6 in. stone. Only when the stone charge is reduced still further does capacity start to increase. Draught varies as the square of capacity. This is because friction varies as the square of velocity, and for double the capacity the friction is four times as great.

A modern kiln with large stone of not unusually crumbly nature will produce about 60 tons of lime from a 60 sq. ft. shaft with a draught of 3 in. The same kiln with the same draught and an automatic draw to loosen the charge and move the fines will produce about 70 tons with 3 in. of draught. In both cases the active height of stone above the gas inlets would be about 37 ft., which would be sufficient for 6 in. stone, but would be far too much for stone of 3 in. or less. If the stone were half the size, and 60 or 70 tons capacity were desired, the draught would have to be increased to 12 in., which for lime kilns is an impracticable figure. Power demand would be excessive, but the gases would be derived through an unnecessarily high bed. If the charge were reduced by half the necessary draught would also be reduced by half, and 6-in. draught is not unreasonably high and not too costly from a power standpoint.

If a 6-in. draught is assumed as the maximum practicable and the height of the stone is 18 ft., small stone could be burned successfully with good capacity, but no higher capacity would be obtained than with stone double the size. No benefit is derived from the increased surface of small stone, due to the increased resistance to the flow of gas through small stone. It is not a matter of calcination time, but rather of gas disposal.

It is only if we go still lower in active kiln height charge that the 6-in. draught will produce more than 60 or 70 tons of lime. One could readily calculate the ratio of required shaft to kiln capacity beyond this point, but these figures would mean little as other factors, like stratification of gases flowing at high velocity, might upset calculations. But it is certain that if lime is made at the calcining surface and there is more calcining surface, then if this surface is supplied with the required amount of heat more lime will be made. It therefore becomes apparent that any modern high-capacity kiln intended to produce a ton of lime per square foot area per day with 6-in. stone cannot produce this amount of lime with 3-in. stone. If the kiln is of a low-capacity type producing, say, 1,000 lb. per square foot with large stone, then this capacity can be equalled, or even increased, with 3-in. stone provided the draught is increased. This is possible because such a kiln is not labouring at the limit of practical draught, as is the case with the high-capacity kiln.

Assuming, for example, the modern type of kiln with submerged offtake and 37 ft. high shaft, for lump lime this height is correct when capacity is high. For spalls everything would remain the same, except that at half the height or lower the shaft would have lateral outlets leading to the duct coming from the upper gas offtake.

While operating with spalls everything would be open and most of the gases would leave through the lateral openings, but they would pass up through the kiln and out through the submerged offtake. With this arrangement the stone would arrive at the mid-gas offtake fairly well preheated, and the upper kiln portion would not be entirely wasted. The draught resistance, on the other hand, would be only that proportion of the high to the mid offtake.

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Notes on High-Alumina Cement.

AN interesting paper by Dr. Gabriel A. Ashkenazi dealing with the history, constitution and uses of high-alumina cement, is published in the May, 1941, number of *Pit and Quarry*, from which the following is taken.

Historical.

It was Jules Bied,[1] the chemist of the French cement concern J. and A. Pavin de Lafarge, who discovered the new cement comprising a combination of less basic aluminates of calcium cement and worked out the commercial method of manufacture. His first French patent had been granted in the year 1908, but it was ten years later before the product came on the market. It was named fused cement (*ciment fondu*) because its manufacture involved melting raw materials in contrast to Portland cement where the raw materials are heated only to the point of clinkering.

The application for a British patent[14] 1909 claimed a cement "containing relatively little silica, the proportion of lime being defined approximately by the formula SiO_2. $2CaO + Al_2O_3$. CaO." Several years later Bied defined his cement by the general formula x C S + y CA, where the ratio of x:y may vary from 0·25 up to 0·90, thus permitting large variations in its chemical composition.[2]

In the United States P. H. Bates[3] reported experiments with calcium aluminates cement in 1919. In 1921 he described a high-alumina cement clinkered in a rotary kiln.[4] H. S. Spackman's "Alca" natural cements, which appeared on the American market in 1910, do not belong in the category of aluminous cements. They represent a mixture of natural Portland cements with 5 or 10 per cent. of calcium aluminates. According to the date published by Spackman,[5] the addition of this energising material resulted in an increase of tensile strength of about 60 to 100 per cent. In 1926 the Michigan Engineering Experiment Station[6] published an investigation of an American commercial aluminous cement. Some time before D. G. Miller, of the United States Department of Agriculture, testing various brands of cements for their durability in corrosive solutions, investigated the behaviour of an American-made aluminous cement. An exceptionally good resistance to the action of sulphate solutions was established.[7]

Resistance to Corrosive Solutions.

Bied's discovery had been hastened by his studies of the deterioration of Portland cement construction due to the presence of gypsum in the soil and in ground waters. French engineers had long before advanced the theory that the deterioration of cement construction exposed to the action of sulphate-containing water is caused by the formation of calcium-sulpho-aluminate. This compound, due to its large amount of crystal water, takes up a larger volume than the initial constituents of cement, thus causing the deformation of the structure. Inasmuch as calcium-sulpho-aluminate, also called "cement bacillus," is produced by the action of sulphates on calcium hydroxide, released during the

hydration of Portland cement, and the ensuing reaction of the so-formed calcium sulphate with the hydrated calcium aluminates, cementing material which would react with water without liberating calcium hydroxide should be more resistant to corrosion. This reasoning led Bied to the invention of aluminous cement, a product not containing the higher calcium silicates and chiefly consisting of less basic calcium aluminates. The fact that the latter compounds, such as CA and C_3A_5, develop high strength has been known.

The early strength of aluminous cement is due to the presence of these aluminates; in addition, the absence of calcium hydrate among its products of hydration makes it immune to attacks by sulphate-containing waters. The writer does not share the French opinion regarding the rôle of calcium hydroxide. The better resistance of aluminous cements is due to the precipitation of alumina hydrate rather than to the absence of free calcium hydroxide. In an article in this journal[8] the author has already expressed his views on this subject.

The resistance of this material to corrosive agents is superior to that of other cementing materials. The writer is cognisant of failures, the reasons for which might be manifold. Excess mixing water, too-prolonged mixing, the placing of a large mass of concrete in one operation, unfavourably influence the development of strength. In some cases the aggregate is apparently of great importance. For instance, limestone or calcareous sands must not be used for concrete which may be subjected to the action of acid-containing waters. But even inert materials like siliceous sands, proved to be of different value. Dr. K. Dorsch[9] examined specimens made of aluminous cement and standard sand and similarly prepared specimens of the same cement and Rhine sand. The specimens were cured in aggressive solutions for 500, 700, and 900 days. Despite the fact that the two kinds of sand could not be affected by the corrosive agents, the specimens made with Rhine sand proved to be more resistant.

Heat of Hydration.

Although the total amount of heat of hydration does not substantially exceed that of Portland cement, it is developed in a very short period. The greater part of it is released during the first ten hours; practically the total amount is generated during the setting time of the cement. In some countries the setting time is determined on a cement paste of normal consistency by following the temperature rise of the paste, the end of the setting being determined by the time when the temperature of the paste reaches a maximum. This property makes possible the use of aluminous cement at low temperatures when concreting with Portland cement is impossible. The writer is aware of concrete and reinforced concrete work done at temperatures as low as minus 4 deg. F., and which showed satisfactory hardening impermeability.

Contrary to the ability of aluminous cement to harden at temperatures below freezing, its resistance is strongly affected at temperatures higher than 100 deg. F. For instance, concrete made with French aluminous cement showed a sharp decrease in strength when stored in water of 158 deg. F.[10]

There are various explanations of this peculiar behaviour. This sharp falling

off in strength at higher temperatures occurs only when aluminous cement concrete is cured in water. In dry heat it preserves properties. This writer, when working in Palestine, had opportunities of examining several aluminous cements of different origin. Laboratory tests as a rule showed very satisfactory results, though the temperature conditions of mixing and curing were not quite favourable. The mixing and curing rooms were not air-conditioned and during several months the inside temperature was seldom below 90 deg. F. Nevertheless, no deviations from the normal development of strength or other properties could be observed. Constructions made in summer, when daily temperatures of over 100 deg. F. were usual, showed no signs of failure during many years. Piles of reinforced concrete made under the burning sun were removed from the forms 24 hours after placing, and two days later had been driven.

Refractory Properties.

Very high dry heat does not affect the binding properties of aluminous cement. It is a well-established fact that, used as a binder of suitable aggregates, it produces a refractory concrete good for service at temperatures of 2,300 deg. F. and higher. Hardened aluminous cement starts to melt at 2,350 deg. F. It is true that its hydraulic binding properties must be destroyed at this temperature, but its binding strengths do not vanish, because before this destruction takes place a new process of hardening is started, a kind of vitrification, similar to that of ceramic material.

The ability of aluminous cement to act as a binder at high temperatures will create a wider market for this product. Furnace walls, for example, may be cast in place; the high early strength allows the application of the full working load 24 hours after placing; the installation of walls without joints results in operating economy, and so forth.

Mixing Aluminous-Cement Concrete.

An excess of mixing water strongly affects the development of strength. For instance, concrete made with a water-cement ratio equal to 0·7 develops, at the age of 24 hours, only two-thirds of the strength of concrete with the ratio of 0·5. However, aluminous cements containing 40 per cent. and more of alumina are less sensitive to an excess of water and are more suitable for poured concrete and grouting. Prolonged mixing is harmful. The producers of American aluminous cement recommend that the time of mixing shall not exceed 1½ minutes. The writer, however, is aware of other brands where the increased time of mixing from 2½ up to ten minutes resulted in a considerable increase of early strength.

Method of Manufacture.

Nearly all countries are applying the melting process in the manufacture of aluminous cement. Different kinds of kilns are used, including reverberatory open-hearth furnaces, rotary kilns and electric furnaces. For bauxites containing a greater amount of iron, blast-furnaces are used, iron being a by-product. The manufacture of aluminous cement, however, does not necessarily require the melting of the raw materials. Bauxites and lime can completely combine when

heated at a temperature of about 1,850 deg. F. for several hours, provided that they are ground to a fineness of 7 per cent. residue on the 180-mesh sieve and that the raw meal possesses a very homogeneous chemical composition. An aluminous cement produced by this method in Hungary complies with the requirements regarding the composition and the development of strength.

Chemical Composition.

The chemical composition of aluminous cements varies considerably. Theoretical considerations permit of Al_2O_2 content ranging from 30 to 70 per cent. The French specification fixes a minimum of 30 per cent. However, as a rule specifications do not standardise the proportions of the main constituents. The content of magnesia, sulphur tri-oxide, and insolubles is limited by some specifications.

The hardening properties of aluminous cements are produced by calcium aluminates. Hence, it has been properly proposed to specify this material as " calcium aluminates " cement to distinguish it from Portland cements belonging to the category of " calcium silicates " cements. The commercial product, however, also contains a considerable amount of iron and silica. The general tendency is to use raw materials containing as little silica as possible. The silica in the various existing commercial aluminous cements usually does not exceed 6 per cent., although there are brands containing up to 10 per cent. The amount of iron in different states of oxidation varies from 5 to 20 per cent. ; that of lime ranges between 25 and 45 per cent. Besides these oxides and small amounts of magnesia and alkalis, titania is usually present in proportion of about 2 per cent.

With respect to its major constituents commercial aluminous cement comprises a complex system—CAO-$Al_2O_3Fe_2O_3$-SiO_2. The knowledge of this quaternary system is not yet sufficiently advanced. The presence of solid solution in aluminous cement increases the difficulties of examination. However, it is generally agreed that, apart from iron compounds, the crystalline ingredients of aluminous cements are represented by mono-calcium aluminate, 5 : 3 calcium aluminate, di-calcium silicate, di-calcium-alumina silicate (Gehlenite), and 3 : 5 calcium aluminate. According to the earlier investigations, C_3A_5 will play an important rôle in producing binding strength. Dr. N. Sundius[11] could not establish the presence of this compound, except in negligible proportions. All agree, however, that mono-calcium aluminate is chiefly responsible for the development of the early strength of aluminous cements. Dr. F. M. Lea[12] states that 1 : 3 mortar made with this compound (water-cement ratio equal to 0 : 6) showed resistance to compression of 8,715, 10,140 and 10,770 lb. per square inch at the age of 1, 7 and 28 days respectively. It should be mentioned that Dr. Sundius describes an aluminous cement consisting chiefly of 5 CaO. 3 Al_2O_3 in a proportion of about 80 per cent.

This so-called unstable 5 : 3 calcium aluminate is easily recognised by microscopic examination of thin sections. In commercial cements it exists not as

pure compound but contains other compounds in solid solution. The same is to be said of other constituents ; the prevalence of solid solutions is characteristic of aluminous cements. With respect to the iron compounds, there are no definite results as to their composition. They form the dark ground glass-like mass in which other minerals are embedded. B. Tavasci, who is of the opinion that this ground mass if mainly Fe_3O_4, states, however, that iron also occurs as C_2F, C_4AF, CAF_2 in the form of solid solutions. The presence of iron combinations and the prevalence of solid solutions complicate the application of methods of investigation which proved efficient in studies of the constitution of Portland cement.

More distinct is the interpretation of the hydration process of aluminous cements. It has been assumed that the reactions of anhydrous calcium aluminates are correlated to those of cement. A series of investigations established a more or less close relationship between the reactions of artificially-prepared pure constituents and those of the commercial product, especially when greater quantities of water were used. In practice, however, the hydration of cement takes place with a small quantity of water. The amount of water changes the course of the reactions. With respect to pure calcium aluminates it has been established that the Ca-concentration of the produced solutions is lower and the Al-concentration is greater when the hydration proceeds in the presence of small amounts of water. Besides, other ingredients of commercial cement also influence the course of hydration. The influence of alkalis[13] proved to be of importance, but the other compounds existing in aluminous cement apparently affect the conditions too. These facts are sufficient to stress the difference between the behaviour of pure aluminates and commercial cements. The hydration reactions of the latter necessarily show an analogy with those of pure constituents, but a complete agreement between them does not exist. The changes caused by the complex character of the cements may be far-reaching ; nevertheless the hydration reaction of anhydrous calcium aluminates is still the most important evidence for the interpretation of the hydration of aluminous cements.

The most important constituent of aluminous cement is mono-calcium aluminate. At lower temperatures it reacts with water, forming mono-calcium aluminate hydrate. At temperatures above 66 degrees F. dicalcium aluminate hydrate and aluminium hydroxide are formed ; at still higher temperatures dicalcium aluminate hydrate is transformed in tricalcium aluminate hydrate. This transformation causes the decrease in the strength of aluminous cement when cured in water at a higher-than-normal temperature. According to N. Iltchenko and H. Lafama[14] this transformation proceeds as shown in the equation

$$3\ (2CaO.Al_2O_3.7H_2O) = 2\ (CaO.Al_2O_3.6H_2O) + 2\ (Al_2O_3.3H_2O) + 3H_2O.$$

In the opinion of these investigators the released water provokes a break of continuity in the process of hardening, thus resulting in a rigorous fall of resistance. Dr. F. M. Lea states that " there is strong evidence that the reduced strength

resulting from higher-than-normal curing temperature is caused by the transformation of metastable less basic hydrated calcium aluminates into the tricalcium aluminate hexahydrate." For a better understanding of the process of hydration we ought to consider it as consisting of two stages. The first stage has chiefly the character of solution; the second comprises the formation of the hydrated compounds.

In the case of pure calcium aluminates the solution consists of mono-calcium aluminate hydrate with a certain excess of lime. The little excess of lime is necessary in order to make this solution stable. Less basic compounds, like C_2A_5, for instance, must yield their excess of alumina. The latter, in the form of aluminium hydroxide, forms a layer on the surface of the grain subjected to the action of water. This coating acts as a de-activating agent; it makes the further action of water more difficult. Therefore, the compound C_3A_5 reacts slowly with water. Consequently calcium aluminates richer in calcium must react faster. In fact, the compound C_5A_3 reacts very rapidly with water. When the solutions have reached a certain concentration hydration products are precipitated. When the hydrated solids have been formed, the concentration of the solutions is low and generally decreases to a certain minimum concentration. The later hydration of the clinker grains therefore depends on the reactions in the diffusion layer at the phase-limit. When pure anhydrous compounds are used, the hydration products can be estimated rather easily. On the other hand, the complex system of the technical cement is more difficult to estimate.

From a practical viewpoint the reactions of pure calcium aluminates, although important for an understanding of the hydration of aluminous cements, do not mirror those taking place in commercial product. The pure dicalcium-alumina silicate (Gehlenite), for example, reacts very slowly with water. The same compound in the commercial aluminous cement, on the contrary, reacts rapidly.[16] It is well known that dicalcium silicate hydrates slowly. According to Lerch and Bogue, its rate of hydration is about 0·1 per cent. in one day, and much unhydrated material is found after two years.[17] The same compound in aluminous cements hydrates fast and probably almost completely.

The chief reactions of calcium aluminates, however, have always been established in the commercial cements. The principal product is the hydrated monocalcium aluminate gel. The hydration products also include the crystalline dicalcium aluminate hydrate and at higher temperatures the cubic tricalcium aluminate hexahydrate is formed. The latter accounts for the peculiar decrease in strength resulting from water curing at higher than normal temperatures.

In contrast to Portland cement—whose grains hydrate gradually and slowly, so that after a considerable period only a part of the cement grain is hydrated—aluminous cement rapidly reacts with water. Most of its grains are transformed into gel. Only the dark glass-like ground mass is not hydrated. This nearly-complete hydration of aluminous cement particles is responsible for the development of early strength. The greater proportion of the hydration products

consists of gels. According to Kühl and Berchem, cement clinker containing 7·5 per cent. of SiO_2, 46·8 per cent. of Al_2O_3 and 41·9 per cent. of CaO produced a gel composed of 2·6 per cent. of silica, 59 per cent. of alumina and 38·4 per cent. of lime. The proportions of lime and alumina are in accord with the expected formation of monocalcium aluminate gel, showing an excess of lime amounting to about 6 per cent. An excess of lime is necessary in order to make possible the existence of monocalcium aluminate in solution. The amount of silica, however, does not correspond to the content of this compound in the cement. The data established by Kühl cannot be generalised. The character of gels depends primarily on the chemical composition of the cement clinker, but also to a great extent upon the mineralogical structure of it. The gels are transformed into solid compounds during the period of stiffening and hardening. The character of these transformations is entirely obscure.

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